

PEM Stack Performance Diagnostics at Los Alamos National Laboratory

Kirk Weisbrod, Jim Lee, Trung Van Nguyen**, Ken Stroh, and Nick Vanderborgh*
MS J576, Los Alamos National Laboratory, Los Alamos NM 87545
(505) 665-7847, fax: (505) 667-0600

* Currently with General Motors, ** Currently Department of Chemical and Petroleum Engineering, University of Kansas, Lawrence

Objectives

- Improve understanding of stack operation through combination of modeling and experiments that include:
 - Two-phase (gas, liquid water) fluid transport under simulated fuel cell conditions.
 - Stack operation on dilute hydrogen and reformat (no contaminants including CO)
 - Temperature distributions in stack during air addition

Approach

- Understand PEM fuel cell stack design options and the influence of such options on fuel cell stack performance.
- Understand options for improving fuel cell stack performance.

Accomplishments

- Initial experiments which visualize 2-phase under simulated stack conditions have been completed.
- The 2-D LANL stack engineering fuel cell model has been expanded to now include anode kinetics for the oxidation of hydrogen under a wide variety of test conditions. Experimental results are compared to predictions.

Future Directions

- Integrate the 2-phase flow results with results emanating from segmented electrode test fixtures to better understand flow field effects.
- Develop a range of advanced diagnostics that lead to understanding transient, three dimensional performance in operating PEM stacks.

Introduction

This report describes FY98 technical progress on fuel cell performance diagnostics. These efforts included both advanced measurements and enhancement in modeling capability. The objective of the two dimensional modeling activity is to predict MEA performance under a wider range of operating conditions. Earlier most modeling activity assumed rapid kinetics on the anode electrode layer, with most performance loss at the air electrode. This often is not the case when operating with reformat fuels. Actual stack

performance at times will be lower than predicted by the 2-D model. Some performance loss may result inadequate gas distribution in the flow fields, for example.

Two Phase Flow Visualization

Fuel cell developers have explored many different technical approaches to achieve uniform, controlled gas distribution across the reacting electrode layer. PEM fuel cell operation necessarily involves two phase water conditions, and liquid water is able to influence flow dynamics. Consequently one emphasis was to observe fundamental properties of the two phase flow condition. A flow visualization test fixture was designed to replicate some of the conditions (flow field design, steam and liquid water flow rates, reactant gas flow rates, temperature, pressure) experienced during actual fuel cell operation. This fixture was designed to permit observation of the interaction of two-phase flow upon the degree of flow uniformity across the surface. Cell layout is shown schematically in Figure 1.

Considerable effort was made to find materials that could result in a credible visualization experiment. After detailed consultation with Energy Partners leading to a design of the visualization test fixture, a commercial water permeable polymer (reverse osmosis) membrane was selected that provided the anticipated water flux rate to simulate water production of an 1 A/cm² operating fuel cell. The experiment utilized specific flow fields made from transparent materials which were in contact with the polymer membrane. (These components were supplied by Energy Partners.) With the flow channels in a horizontal orientation, experiments were performed with an air flow rate corresponding to a stoichiometry between 2 to 3 with 1 psi pressure drop at 30 ft/s flow velocity across the flow field. Slug or plug flow was not observed. *Annular flow* was observed with water flowing as a thin sheet along the walls while gas occupied the center of the channel. This was not an anticipated result and suggests that even under these modest flow conditions, liquid water and reactant gases can move at different velocities. No channel blocking (stagnant liquid water) was observed.

These observations were compared to literature correlation which have been made describing two phase flow. For horizontal flow, Baker (1954) predicted that wave to annular flow will occur. A correlation by Taitel (1976) showed that an annular-dispersed liquid regime should exist. In that case liquid is predicted to occupy 10 to 15% of the cross-sectional area. For vertical flow in the upward direction, a frothy to film flow is predicted by Govier et al (1957). Finally under microgravity conditions, applicable for space operation, a frothy liquid or annular type flow is again predicted (Zhao, 1993).

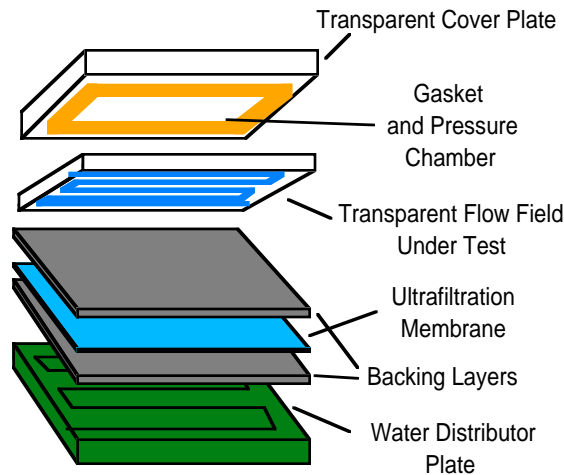


Figure 1. Expanded view of flow visualization hardware for studying water removal parameters. Liquid water is pumped into the “water distribution plate” and through the “ultrafiltration membrane” where it enters uniformly across the flow plane. Gases are fed into the transparent flow field and the resulting flow is observed through the “transparent cover plate”. Varying the pressure in the water distributor plate mimics the current density—more or less product water is produced per unit area. Steam can be added to the reactant gas to account for operation with humidified reactants.

Flow field options include serpentine, inter-digitated, parallel groove and porous flow field designs. The combination of a segmented electrode with a flow visualization cell may prove most beneficial in exploring flow regimes on a case by case basis, electronic although conduction features are required when working with actual fuel cells.

Mathematical Analysis of Fuel Cell Operation

The 2-D model presented previously as part of the Fuel Cell Engineering research included transport of both reactant gases and water, as well as ionic conductivity of the cathode catalyst layer and membrane. The model is based upon first principles utilizing parameter values derived from independent sources and measurements. The latest version of the through-the-electrode component of the model is illustrated in Figure 2.¹

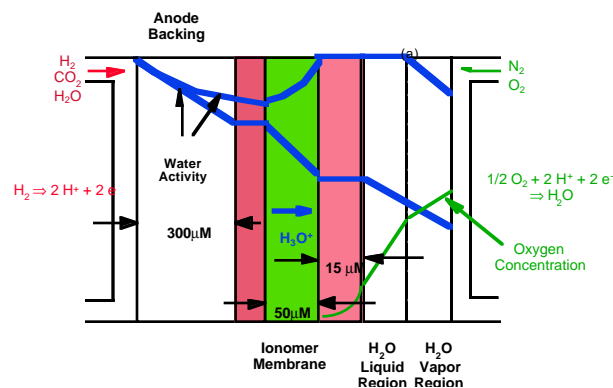


Figure 2. Schematic of through-the-electrode components of the 2-D model. The fuel cell zone is segmented into 6 layers, from the anode to cathode side. The two cathode porous layers allow for separate treatment of an “inner” water saturated layer and an outer layer.

The 2-D model also calculates changes in MEA performance in the flow direction (“along the channel”, but more correctly in regions of various reactant utilization conditions) by accounting for changes in gas composition from consumption of reactants, water production, and water transport through the MEA. Recently we added dynamic features of an novel anode catalyst layer which include gas transport, ionic resistance within the layer and hydrogen oxidation kinetics both in the presence and absence of CO_2 . Poisoning from CO and other adsorbates along with discrete chemical processing within the anode compartment will be added subsequently.

The model was validated utilizing data obtained on a thin film catalyst layer of supported platinum.² The exchange current density for hydrogen oxidation was adjusted to $2,000 \text{ A/cm}^2$ at 22°C to match the 0.05 volt overpotential reported previously in the literature observed under pure hydrogen conditions. Model predictions are shown for pure hydrogen and hydrogen diluted with 25% CO_2 where it is assumed that 80% of the catalyst surface area is covered with a “reduced CO_2 ” species. Finally, CO_2 adsorption is turned off to simulate the effects of 2% air addition. While the model results tend to predict better performance than observed experimentally when pure H_2 is investigated, the relative predicted performance adequately reflects the observed experimental trend—this approach tends to afford excellent predictability. Thus, with the given electrode configuration, a decrease in electrode performance may be attributed to formation of a “reduced CO_2 ” species.

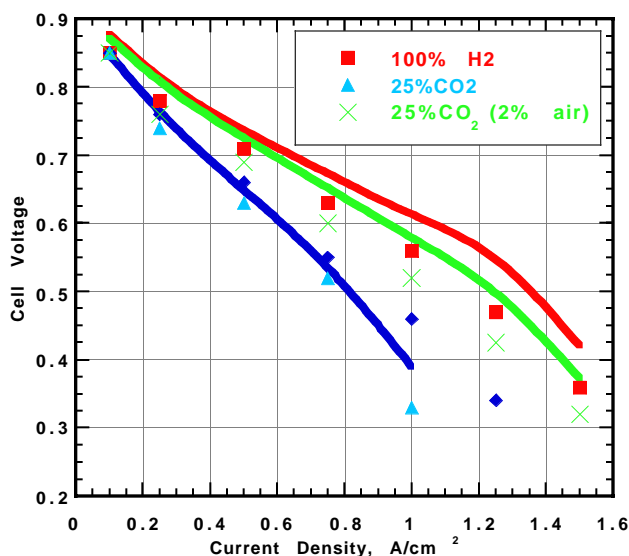


Figure 3. H_2 /air PEFC polarization curves for thin film Pt electrode with 0.14 mg Pt/cm^2 . Curves are predictions for 100% H_2 , 25% CO_2 and 25% CO_2 with adsorption dynamics turned off.²

Others (Zawodzinski, et al., at LANL mid-year review) reported cell performance with Pt-Ru alloy catalyst on reformat without any added CO. The thesis was that decreased performance on reformat results from insufficient humidification of the reformat gas stream. This was simulated assuming the anode humidifier operated at 80°C and resulted in 60% RH. A comparison between the experimental and predicted results is illustrated in Figure 4.

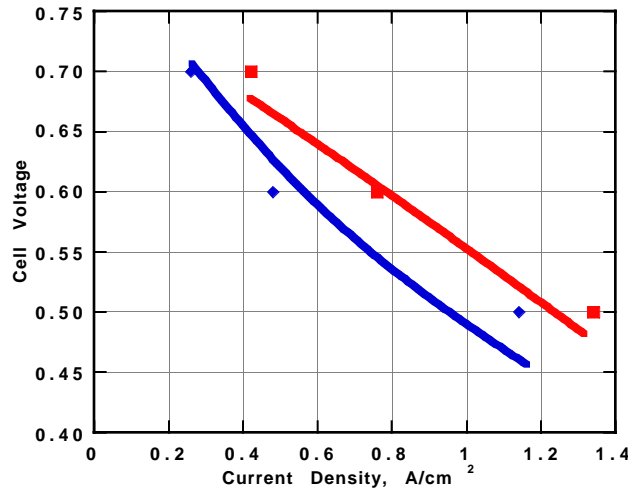


Figure 4. Simulated reformate (no CO) / air performance: 50 cm² cell, Nafion 1135, 80°C cell, assuming 80°C humidifier temperature, Anode: Type 1 with 0.5 mg PM/cm², H₂/N₂/CO₂ 40/35/20%, Cathode: 0.3 mg/cm², A/C Stoichiometry 1.5/2.0 at 1.4 A/cm².

Since it was previously shown that a Pt-Ru catalyst can eliminate the effects of CO₂ adsorption², this performance loss mechanism was turned off during the simulation. Thus the decrease in performance may be attributed primarily to dehydration effects with only a minor dilution effect.

This mathematical tool can also describe the impact of electrode structure under observed fuel cell performance. For example, the performance of a Ballard Mark 5 stack was simulated when operated with hydrogen feed diluted with nitrogen. The stack was modeled assuming ionic conductivity of the electrodes results from the incorporation of 6 wt% ionomer within the anode electrode layer. Based upon extensive, previous experience with membrane humidifiers, stack humidification was set to be a function of gas flow rate. In this case as well, the model adequately predicts performance. With this type of electrode structure, hydrogen dilution results in increasing the anode overpotential. Figure 6 shows that the predicted local current density for the anode catalyst layer is significantly different for three cases given above. In the Ballard anode, inadequate ionic conductivity confines the oxidation reaction to only that region close to the membrane. In a thin film anode, a larger fraction of the anode is active with for neat hydrogen oxidation. However under reformate conditions diluted with 25% CO₂, kinetic resistance dominates and results in nearly uniform current distribution throughout the electrode layer thickness.

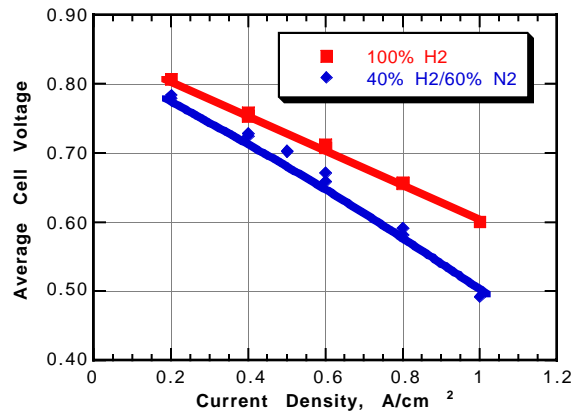


Figure 5. Effect of hydrogen dilution in a Ballard stack: 80°C, A/C 3 atm, A/C Stoichiometry 1.2/2.5, 4 mg Pt black catalyst per electrode.

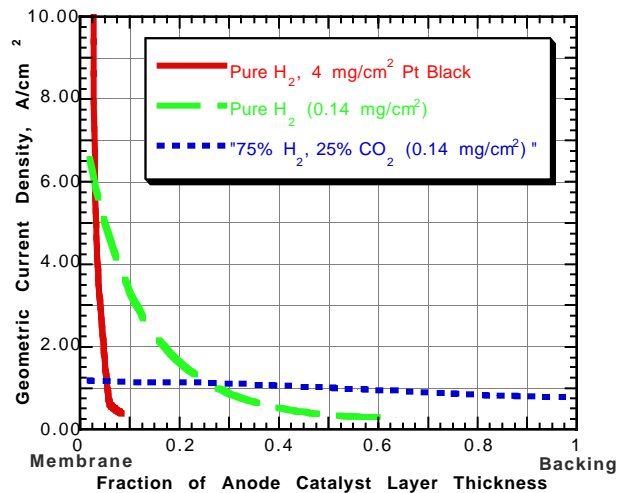


Figure 6. Distribution of local current density through the anode catalyst layer thickness in the condition of reformat dilution (25% CO₂).

REFERENCES

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2. M. Wilson, C. Derouin, J. Valerio and S. Gottesfeld: "Electrocatalysis Issues in Polymer Electrolyte Fuel Cells," IECEC-93, Atlanta, Georgia.